

# IDENTIFICATION OF MULTIPLE-ADDITIVES FOR SYNTHETIC POLYMER USING SPECTRAL DATABASE OF PHOTODIODE ARRAY DETECTOR AND MASS DETECTOR

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## INTRODUCTION

In recent years, it has become a challenge to understand the impact on the quality of trace substances such as additives from point of view of product development and quality assurance in polymer materials. In order to accurately identify these compounds, UV spectrum matching using a photodiode array (PDA) detector is used. However, compounds with similar structures may not be accurately identified. In this case, identification by MS spectrum using a mass spectrometer is useful, but in many cases, complicated tuning and complicated analysis operations are required as compared with an optical detector for LC. Waters have developed a quadrupole mass spectrometer (ACQUITY QDa) that does not require complicated tuning, optimization of ionization conditions, and complicated analysis operations. By using a PDA detector together with a compact quadrupole mass spectrometer (QDa) that can obtain information related to the molecular weight with the same size and easy operability as this optical detector, compound identification ability can be achieved. We report the improvement, the detection of compounds that do not have UV absorption (do not have chromophore), and the easier detection.

## METHODS

### 1) LC/MS condition

ACQUITY H-Class (Waters) was used as inlet of LC/MS. Several types of ACQUITY UPLC column were used for investigating the appropriate separation conditions. For the column, various functional groups such as C18, C8, and Phenyl were tested, and a Phenyl column with the best separation of each component was adopted. Optimized LC conditions are shown below.

#### -LC condition -

- Column : ACQUITY UPLC BEH Phenyl  
1.7  $\mu$ m, 2.1x100 nm
- Column Temperature : 40 C
- Mobile phase A : 100mM-Ammonium bicarbonate aq  
(containing 2.5%-ammonia)
- Mobile phase B : Acetonitrile
- Mobile phase C : Water
- Gradient :

Time	%A	%B	%C	Curve
0.00	3.00	45.00	52.00	
15.00	3.00	94.00	3.00	6
18.00	3.00	45.00	52.00	1

- flow rate : 0.6 mL/min
- PDA : 200 to 400 nm (extraction at 220 nm)-  
18 min (including equilibration time)

ACQUITY QDa detector was used as Mass spectrometer. QDa detector, it has the same size and compactness as an optical detector, but has the functions of a mass spectrometer. Furthermore, it is an "MS detector for chromatographers" that can obtain information related to molecular weight without performing the complex tuning and optimization of ionization conditions required for general mass spectrometers. MS conditions are shown below, and a schematic diagram is shown in Fig. 1.

- Desolvation gas Temp. : 600 C

Mode	Polarity	Capillary Voltage (kV)	Cone Voltage (V)	Mass range (Da)
MS scan	Positive	1.5	15	200 - 1220
MS scan	Negative	0.8	15	300 - 800

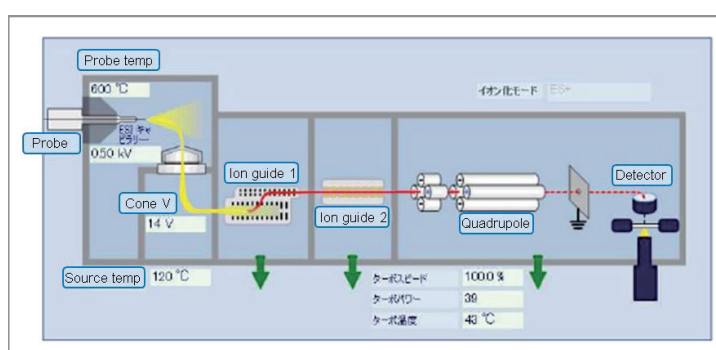


Figure 1. Schematic diagram of QDa mass detector

### 2) Polymer additives database

Separation conditions of the 32 additives listed in Table. 1 were examined.

The UV and MS spectra obtained under the final analytical conditions were registered in the software, and an additive database for synthetic polymer was constructed.

	Compound	Rt(min)	UV	m/Z	Ion
1	SanoLS744	1.6		262.2	M+H
2	Tinuvin P	2.4		226.1	M+H
3	Irganox1222	2.5		357.2	M+H
4	Tinuvin292_1	3.7	x	370.3	M+H
5	SanoLS770	4.2	x	481.5	M+H
6	SanoLS440	4.8		436.4	M+H
7	Irganox245	5.0		604.5	M+NH4
8	IrganoxMD1024	5.4		570.5	M+NH4
9	Irganox1098	6.0		637.6	M+H
10	Tinuvin329	6.4		324.2	M+H
11	Irganox1081	6.7		357.2	M-H
12	Tinuvin292_2	6.8	x	509.4	M+H
13	Tinuvin326	6.9		314.0	M-H
14	Tinuvin510	7.2		340.2	M+H
15	Tinuvin320	7.3		324.2	M+H
16	Tinuvin327	8.4		356.2	M-H
17	Tinuvin328	8.5		352.2	M+H
18	Tinuvin120	8.7		439.3	M+H
19	Tinuvin234	8.8		448.3	M+H
20	Irganox1035	9.2		660.5	M+NH4
21	Tinuvin1577FF	9.4		426.3	M+H
22	Tinuvin928	9.7		442.3	M+H
23	Irganox259	9.8		656.6	M+NH4
24	Tinuvin144	10.6		685.7	M+H
25	Irganox3114	11.1		801.6	M+NH4
26	SanoLS2626	11.2		722.7	M+H
27	Irganox565	12.4		589.5	M+H
28	Irgafos168_Oxi	12.6		663.6	M+H
29	Irganox1076	12.7		529.5	M-H
30	Irganox1330	12.9		792.7	M+NH4
31	Irganox1010	13.2		1195.1	M+NH4
32	Irgafos168	13.6		647.6	M+H
33	Tinuvin152	13.9		757.8	M+H
34	TINUVIN123	14.7	x	737.8	M+H

Table 1. Additive list for synthesized polymer

### 3) Extraction from polymer products

Extraction was operated with supercritical fluid extraction (SFE) from general-purpose polypropylene bag. Extraction solvent was measured with optimized analytical method. In the SFE system, the extraction time was as short as 30 minutes compared with the soxhlet extraction and the reprecipitation method, and residual oligomer could be selectively removed.

- Modifier : Methanol/CO2 (20%/80%)
- Flow rate : 10 mL/min
- Temperature : 60 C
- Back pressure (ABPR) : 200 Bar
- Extraction time : 30 min
- Make up solvent : Acetone (1.5 mL/min)

## RESULTS

### Separation of additive standard

Figure 2 shows the UV and MS chromatograms obtained with final conditions. Analytical method to separate 32 additives including components with no chromophore was established with in 15min run time. With this analytical condition, all 32 components could be completely separated and detected.

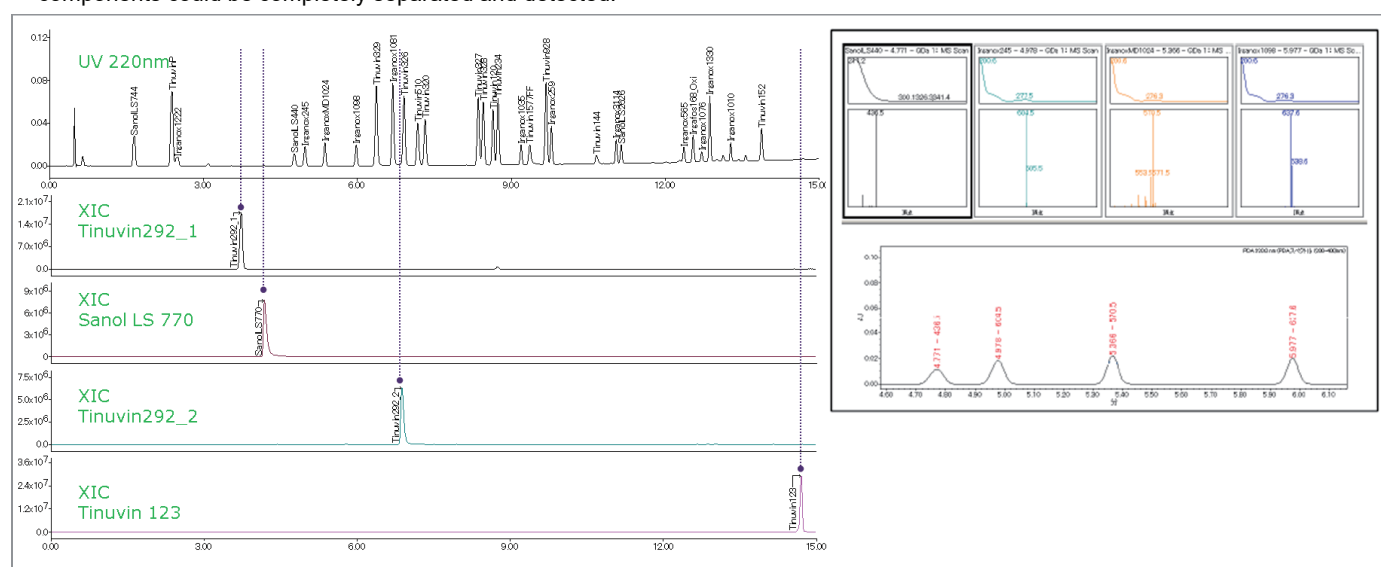


Figure 2. UV chromatogram and mass chromatogram of 32 Polymer additives (Left) Aligned UV and mass spectrum of registered additives in database (Right)

### Identification of additives in sample through spectrum database

Fig. 3 shows the UV chromatogram of polymer additive mixture standard and SFE extraction sample. In spectral database search, it is possible to perform spectral database search of additives detected in UV chromatogram for both UV and MS. When only UV spectrum database was used for identification, additives with similar structure, close retention time, and same chromophore had been misidentified. However by leveraging MS spectrum for identification, there was no misidentification, accuracy and probability of unknown additive identification was improved.

## CONCLUSION

Separation method of 32 polymer additives was developed, and this enabled to identify unknown additives in polymer materials by searching the database by combining not only UV spectra but also MS spectra.

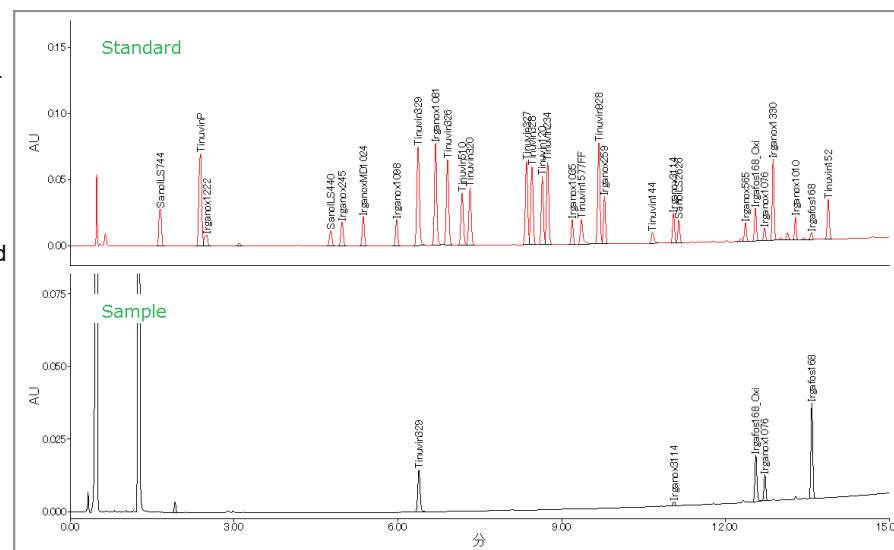


Figure 3. UV chromatogram of additive standard and sample extracted with SFE